

The Claims

What is claimed is:

- 5 1. A post CMP cleaning formulation comprising an organic amine, a fluoride source and from 70% to 98% water.

2. The post CMP cleaning formulation according to claim 1, wherein said formulation further comprises a metal chelating agent.

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3. The post CMP cleaning formulation according to claim 2, wherein said formulation further comprises a nitrogenous component.

- 15 4. The post CMP cleaning formulation according to claim 1, wherein said fluoride source comprises from about 0.1% to about 5.0% of the formulation.

5. The post CMP cleaning formulation according to claim 1, wherein said fluoride is selected from the group consisting of:

- 20 any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid,
 ammonium fluoride,

- ammonium bifluoride,
triethanolammonium fluoride, (TEAF),
diglycolammonium fluoride, (DGAF),
tetramethylammonium fluoride, (TMAF),
5 methyl-diethanolammonium fluoride, (MDEAF) and
triethylamine tris (hydrogen fluoride) (TREAT-HF).

6. The post CMP cleaning formulation according to claim 1, wherein said formulation comprises from about 1% to 15% organic amine.

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7. The post CMP cleaning formulation according to claim 1, wherein said organic amine is selected from the group consisting of:

- diglycolamine (DGA),
methyldiethanolamine (MDEA),
15 pentamethyldiethylenetriamine (PMDETA),
triethanolamine (TEA),
triethylenediamine (TEDA),
hexamethylenetetramine,
3, 3-iminobis (N,N-dimethylpropylamine),
20 monoethanolamine.

2-(methylamino)ethanol,

4-(2-hydroxyethyl)morpholine

4-(3-aminopropyl)morpholine, and

N,N-dimethyl-2-(2-aminoethoxy)ethanol.

- 5 8. The post CMP cleaning formulation according to claim 2, wherein said formulation comprises from about 0 to about 5.0 % metal chelating agent.

9. The post CMP cleaning formulation according to claim 2, wherein said metal chelating agent is selected from the group consisting of:

- 10 acetoacetamide;
- ammonium carbamate;
- ammonium pyrrolidinedithiocarbamate (APDC);
- dimethyl malonate;
- methyl acetoacetate;
- 15 N-methyl acetoacetamide;
- 2,4-pentanedione;
- 1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfac);
- 2,2,6,6-tetramethyl-3,5-heptanedione H(thd);
- tetramethylammonium thiobenzoate;
- 20 tetramethylammonium trifluoroacetate;

- tetramethylthiuram disulfide (TMTDS);
- trifluoroacetic acid;
- lactic acid;
- ammonium lactate;
- 5 malonic acid
- formic acid,
- acetic acid,
- propionic acid,
- gamma-butyrolactone,
- 10 methyldiethanolammonium trifluoroacetate, and
- trifluoroacetic acid.

10. The post CMP cleaning formulation according to claim 3, wherein said formulation comprises from about 0 to about 10 % nitrogenous component.

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11. The post CMP cleaning formulation according to claim 3, wherein said nitrogenous component is selected from the group consisting of:

- iminodiacetic acid (IDA),
- glycine,
- 20 nitrilotriacetic acid (NTA),

hydroxyethyliminodiacetic acid,

1,1,3,-tetramethylguanidine (TMG),

ethylenediaminetetracetic acid (EDTA),

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,

5 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,

$\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,

$(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$.

$\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$, and

$\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$.

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12. The post CMP cleaning formulation according to claim 1, wherein said formulation comprises:

triethanolamine	4.5 %,
ammonium Fluoride	0.5 %, and
15 water	95 %.

13. The post CMP cleaning formulation according to claim 1, wherein said formulation comprises:

PMDETA	3.8-4.5 %,
20 ammonium fluoride	0.5 %,

2, 4-Pentanedione 1 %, and
water 94-94.7 %.

14. The post CMP cleaning formulation according to claim 1, wherein said formulation
5 comprises:

TEA 1.7 %
PMDETA 1.5 %
TEAHF 2 %,
iminodiacetic Acid 0.4 %,
10 ammonium bifluoride 0.5 %, and
water 93.9 %.

15. The post CMP cleaning formulation according to claim 1, wherein said formulation
comprises:

15 TEA 3.5 %,
PMDETA 1.5 %,
2, 4-Pentanedione 1.35 %,
ammonium fluoride 1.2 %, and
water 92.45 %.

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16. The post CMP cleaning formulation according to claim 1, wherein said formulation comprises:

	TEA	7 %,
	PMDETA	3 %,
5	2, 4-Pentanedione	2.7 %,
	ammonium fluoride	2.4 %, and
	water	84.9 %.

10 ☒ 17. A semiconductor wafer cleaning formulation comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

	fluoride source	1-35%
	organic amine(s)	20-60%
	a nitrogenous component, selected from nitrogen-containing carboxylic acids and	
15	imines	0.1-40%
	water	20-50%
	<u>metal chelating agent(s)</u>	<u>0-21%</u>
	TOTAL	100%

18. The cleaning formulation of claim 17, wherein said fluoride source comprises a fluoride species selected from the group consisting of:

any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid;

5 ammonium bifluoride;

ammonium fluoride,

triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),

tetramethylammonium fluoride (TMAF),

10 methyldiethanolammonium fluoride (MDEAF) and

triethylamine tris (hydrogen fluoride) (TREAT-HF)..

19. The cleaning formulation of claim 17, wherein said organic amine(s) comprise an amine selected from the group consisting of:

15 diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA),

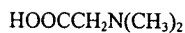
triethylenediamine (TEDA),

20 hexamethylenetetramine,

- 3, 3-iminobis (N,N-dimethylpropylamine),
 monoethanolamine.
 2-(methylamino)ethanol,
 4-(2-hydroxyethyl)morpholine
 5 4-(3-aminopropyl)morpholine, and
 N,N-dimethyl-2-(2-aminoethoxy)ethanol.

20. The cleaning formulation of claim 17, wherein said nitrogenous component comprises a species selected from the group consisting of:

- 10 iminodiacetic acid (IDA)
 glycine
 nitrilotriacetic acid (NTA)
 hydroxyethyliminodiacetic acid
 1,1,3,-tetramethylguanidine (TMG)
 15 ethylenediaminetetracetic acid (EDTA)
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$
 $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$
 $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$



21. The cleaning formulation of claim 17, including at least one metal chelating agent selected
5 from the group consisting of:

acetoacetamide;

ammonium carbamate;

ammonium pyrrolidinedithiocarbamate (APDC);

dimethyl malonate;

10 methyl acetoacetate;

N-methyl acetoacetamide;

2,4-pentanedione;

1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfac);

2,2,6,6-tetramethyl-3,5-heptanedione H(thd);

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tetramethylammonium thiobenzoate;

tetramethylammonium trifluoroacetate;

tetramethylthiuram disulfide (TMTDS);

trifluoroacetic acid;

- lactic acid;
- ammonium lactate;
- malonic acid
- formic acid,
- 5 acetic acid,
- propionic acid,
- gamma-butyrolactone,
- iminodiacetic acid,
- methyldiethanolammonium trifluoroacetate, and
- 10 trifluoroacetic acid.
22. The cleaning formulation of claim 17, wherein said fluoride source comprises a species selected from the group consisting of:
- 15 any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid;
- ammonium fluoride;
- ammonium bifluoride;
- triethanolammonium fluoride (TEAF);
- diglycolammonium fluoride (DGAF),
- 20 methyldiethanolammonium fluoride (MDEAF);

tetramethylammonium fluoride (TMAF); and

triethylamine tris (hydrogen fluoride) (TREAT-HF

23. The cleaning formulation of claim 17, wherein said organic amine(s) comprises an amine
5 selected from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA),

10 triethylenediamine (TEDA),

hexamethylenetetramine,

3, 3-iminobis (N,N-dimethylpropylamine),

monoethanolamine.

2-(methylamino)ethanol,

15 4-(2-hydroxyethyl)morpholine

4-(3-aminopropyl)morpholine, and

N,N-dimethyl-2-(2-aminoethoxy)ethanol.

24. The cleaning formulation of claim 17, wherein said nitrogenous component comprises a
20 species from the group consisting of:

iminodiacetic acid (IDA)

glycine

nitrilotriacetic acid (NTA)

hydroxyethyliminodiacetic acid

5 1,1,3,-tetramethylguanidine (TMG)

ethylenediaminetetracetic acid (EDTA)

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$

$\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$

10 $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$

$\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$

$\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$.

25. The cleaning formulation of claim 17, wherein said fluoride source comprises a species
15 selected from the group consisting of:

any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid;

ammonium fluoride;

ammonium bifluoride;

20 triethanolammonium fluoride (TEAF);

diglycolammonium fluoride (DGAF);

methyldiethanolammonium fluoride (MDEAF)

tetramethylammonium fluoride (TMAF); and

triethylamine tris (hydrogen fluoride) (TREAT-HF);

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said organic amine(s) comprise a species selected from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

10 triethanolamine (TEA),

triethylenediamine (TEDA),

hexamethylenetetramine,

3, 3-iminobis (N,N-dimethylpropylamine),

monoethanolamine.

15 2-(methylamino)ethanol,

4-(2-hydroxyethyl)morpholine,

4-(3-aminopropyl)morpholine, and

N,N-dimethyl-2-(2-aminoethoxy)ethanol;

said nitrogenous component comprises a species selected from the group consisting of:

- iminodiacetic acid (IDA),
- glycine,
- nitrilotriacetic acid (NTA),
- hydroxyethyliminodiacetic acid,
- 5 1,1,3,-tetramethylguanidine (TMG),
- ethylenediaminetetracetic acid (EDTA)
- $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
- $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
- $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,
- 10 $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$,
- $\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$,
- $\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$; and

said formulation includes a metal chelating agent comprising a species selected from the group consisting of:

- 15 acetoacetamide;
- ammonium carbamate;
- ammonium pyrrolidinedithiocarbamate (APDC);
- dimethyl malonate;
- methyl acetoacetate;

- N-methyl acetoacetamide;
- 2,4-pentanedione;
- 1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfac);
- 2,2,6,6-tetramethyl-3,5-heptanedione H(thd);
- 5 tetramethylammonium thiobenzoate;
- tetramethylammonium trifluoroacetate;
- tetramethylthiuram disulfide (TMTDS);
- trifluoroacetic acid;
- lactic acid;
- 10 ammonium lactate;
- malonic acid
- formic acid,
- acetic acid,
- propionic acid,
- 15 gamma-butyrolactone,
- iminodiacetic acid,
- methyldiethanolammonium trifluoroacetate, and
- trifluoroacetic acid.

26. The cleaning formulation of claim 17, wherein said fluoride source comprises a compound having the general formula $R_1R_2R_3R_4NF$ in which each of the R groups is independently selected from hydrogen atoms and aliphatic groups, and wherein said formulation includes a metal chelating agent of the formula:

5 X-CHR-Y,

in which R is either hydrogen or an aliphatic group and X and Y are functional groups containing multiply bonded moieties having electron-withdrawing properties.

27. The cleaning formulation of claim 25, wherein each of X and Y is independently selected
10 from $CONH_2$, $CONHR'$, CN , NO_2 , SOR' , and SO_2Z in which R' is alkyl and Z is hydrogen, halo, or alkyl.

28. The cleaning formulation of claim 17, wherein said fluoride source comprises a compound having the formula $R_1R_2R_3R_4NF$ in which each of the R groups is hydrogen or aliphatic, and
15 wherein said formulation includes a metal chelating agent of the formula, $R_1R_2R_3R_4N^+O_2CCF_3$ in which each of the R groups is independently hydrogen or aliphatic.

29. The cleaning formulation of claim 17, wherein said nitrogenous component includes a compound having the formula:

20 $COOH-CH_2-NRR'$

wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acids.

30. A method for fabricating a semiconductor wafer, comprising:

plasma etching a metallized layer from a surface of the wafer;

plasma ashing a resist from the surface of the wafer; and

5 cleaning the wafer by contacting same with a cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

	fluoride source	1-35%
	organic amine(s)	20-60%
10	a nitrogenous component, selected from nitrogen-containing carboxylic acids and imines	0.1-40%
	water	20-50%
	<u>metal chelating agent(s)</u>	<u>0-21%</u>
	TOTAL	100%

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31. The method of claim 30, wherein said fluoride source comprises a fluoride species selected from the group consisting of:

any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid;

20 ammonium fluoride;

ammonium bifluoride;

- triethanolammonium fluoride (TEAF);
- diglycolammonium fluoride (DGAF);
- methyldiethanolammonium fluoride (MDEAF)
- tetramethylammonium fluoride (TMAF); and
- 5 triethylamine tris (hydrogen fluoride) (TREAT-HF).

32. The method of claim 30, wherein said organic amine(s) comprise an amine selected from the group consisting of:

- diglycolamine (DGA),
- methyldiethanolamine (MDEA),
- 10 pentamethyldiethylenetriamine (PMDETA),
- triethanolamine (TEA),
- triethylenediamine (TEDA),
- hexamethylenetetramine,
- 3, 3-iminobis (N,N-dimethylpropylamine),
- 15 monoethanolamine.
- 2-(methylamino)ethanol,
- 4-(2-hydroxyethyl)morpholine
- 4-(3-aminopropyl)morpholine, and
- N,N-dimethyl-2-(2-aminoethoxy)ethanol.

33. The method of claim 30, wherein said nitrogenous component comprises a species selected from the group consisting of:

- iminodiacetic acid (IDA),
- 5 glycine,
- nitilotriacetic acid (NTA),
- hydroxyethyliminodiacetic acid,
- 1,1,3,-tetramethylguanidine (TMG),
- ethylenediaminetetracetic acid (EDTA),
- 10 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
- $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
- $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,
- $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$,
- $\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$,
- 15 $\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$.

34. The method of claim 30, including at least one metal chelating agent selected from the group consisting of:

- acetoacetamide;
- ammonium carbamate;
- 20 ammonium pyrrolidinedithiocarbamate (APDC);

- dimethyl malonate;
- methyl acetoacetate;
- N-methyl acetoacetamide;
- 2,4-pentanedione;
- 5 1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfac);
- 2,2,6,6-tetramethyl-3,5-heptanedione H(thd);
- tetramethylammonium thiobenzoate;
- tetramethylammonium trifluoroacetate;
- tetramethylthiuram disulfide (TMTDS);
- 10 trifluoroacetic acid;
- lactic acid;
- ammonium lactate;
- malonic acid
- formic acid,
- 15 acetic acid,
- propionic acid,
- gamma-butyrolactone,
- iminodiacetic acid,
- methyldiethanolammonium trifluoroacetate, and

trifluoroacetic acid.

35. The method of claim 30, wherein said fluoride source comprises a species selected from the group consisting of:

- 5 any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid;
- ammonium fluoride,
- ammonium bifluoride,
- triethanolammonium fluoride (TEAF),
- 10 diglycolammonium fluoride (DGAF),
- methyldiethanolammonium fluoride (MDEAF),
- tetramethylammonium fluoride (TMAF), and
- triethylamine tris (hydrogen fluoride) (TREAT-HF).

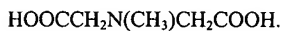
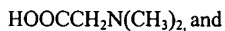
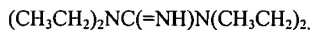
36. The method of claim 30, wherein said organic amine(s) comprises an amine selected from
15 the group consisting of:

- diglycolamine (DGA),
- methyldiethanolamine (MDEA),
- pentamethyldiethylenetriamine (PMDETA),
- triethanolamine (TEA),
- 20 triethylenediamine (TEDA),

- hexamethylenetetramine,
 3, 3-iminobis (N,N-dimethylpropylamine),
 monoethanolamine.
 2-(methylamino)ethanol,
 5 4-(2-hydroxyethyl)morpholine
 4-(3-aminopropyl)morpholine, and
 N,N-dimethyl-2-(2-aminoethoxy)ethanol.

37. The method of claim 30, wherein said nitrogenous component comprises a species from the
 10 group consisting of:

- iminodiacetic acid (IDA),
 glycine,
 nitrilotriacetic acid (NTA),
 hydroxyethyliminodiacetic acid,
 15 1,1,3,-tetramethylguanidine (TMG),
 ethylenediaminetetracetic acid (EDTA),
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
 $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,



- 5 38. The method of claim 30, wherein said fluoride source comprises a species selected from the group consisting of:

any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid,

ammonium fluoride,

- 10 ammonium bifluoride,

triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),

methyldiethanolammonium fluoride (MDEAF),

tetramethylammonium fluoride (TMAF), and

- 15 triethylamine tris (hydrogen fluoride) (TREAT-HF);

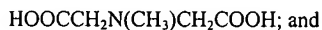
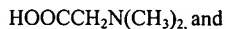
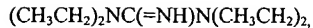
said organic amine(s) comprise a species selected from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

- 20 pentamethyldiethylenetriamine (PMDETA),

- triethanolamine (TEA),
- triethylenediamine (TEDA),
- hexamethylenetetramine,
- 3, 3-iminobis (N,N-dimethylpropylamine),
- 5 monoethanolamine.
- 2-(methylamino)ethanol,
- 4-(2-hydroxyethyl)morpholine
- 4-(3-aminopropyl)morpholine, and
- N,N-dimethyl-2-(2-aminoethoxy)ethanol;
- 10 said nitrogenous component comprises a species selected from the group consisting of:
- iminodiacetic acid (IDA),
- glycine,
- nitrilotriacetic acid (NTA),
- hydroxyethyliminodiacetic acid,
- 15 1,1,3,-tetramethylguanidine (TMG),
- ethylenediaminetetracetic acid (EDTA),
- $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
- $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
- $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,



said formulation includes a metal chelating agent comprising a species selected from the group
5 consisting of:

acetoacetamide;

ammonium carbamate;

ammonium pyrrolidinedithiocarbamate (APDC);

dimethyl malonate;

10 methyl acetoacetate;

N-methyl acetoacetamide;

2,4-pentanedione;

1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfac);

2,2,6,6-tetramethyl-3,5-heptanedione H(thd);

15 tetramethylammonium thiobenzoate;

tetramethylammonium trifluoroacetate;

tetramethylthiuram disulfide (TMTDS);

lactic acid;

ammonium lactate;

malonic acid

formic acid,

acetic acid,

propionic acid,

5 gamma-butyrolactone,

methyldiethanolammonium trifluoroacetate, and

trifluoroacetic acid.

39. The method of claim 30, wherein said fluoride source comprises a compound having the
10 general formula $R_1R_2R_3R_4NF$ in which each of the R groups is independently selected from
hydrogen atoms and aliphatic groups, and wherein said formulation includes a metal chelating
agent of the formula:

$X-CHR-Y$,

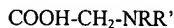
in which R is either hydrogen or an aliphatic group and X and Y are functional groups
containing multiply bonded moieties having electron-withdrawing properties.

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40. The method of claim 39, wherein each of X and Y is independently selected from $CONH_2$,
 $CONHR'$, CN , NO_2 , SOR' , and SO_2Z in which R' is alkyl and Z is hydrogen, halo, or alkyl.

41. The method of claim 30, wherein said fluoride source comprises a compound having the
20 formula $R_1R_2R_3R_4NF$ in which each of the R groups is hydrogen or aliphatic, and wherein said
formulation includes a metal chelating agent of the formula, $R_1R_2R_3R_4N^+O_2CCF_3$ in which
each of the R groups is independently hydrogen or aliphatic.

42. The method of claim 30, wherein said nitrogenous component includes a compound having the formula:



- 5 wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acids.

~~43.~~ A method for fabricating a semiconductor wafer including the steps comprising:

plasma etching a metallized layer from a surface of the wafer;

- 10 plasma ashing a resist from the surface of the wafer;

cleaning the wafer by contacting same with a cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

	a fluoride source;	1-35%
15	at least one organic amine;	20-60%
	a nitrogen-containing carboxylic acid or imine	0.1-40%
	water;	20-50%
	<u>at least one metal chelating agent</u>	<u>0-21%</u>
	TOTAL	100%.

20

44. The method of claim 43, wherein said fluoride source is chosen from the group consisting of:

any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid,

5 ammonium fluoride,

ammonium bifluoride,

triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),

methyldiethanolammonium fluoride (MDEAF),

10 tetramethylammonium fluoride (TMAF), and

triethylamine tris (hydrogen fluoride) (TREAT-HF).

45. The method of claim 43, wherein said organic amine is selected from the group consisting of:

15 diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA),

triethylenediamine (TEDA),

20 hexamethylenetetramine,

- 3, 3-iminobis (N,N-dimethylpropylamine),
 monoethanolamine.
 2-(methylamino)ethanol,
 4-(2-hydroxyethyl)morpholine
 5 4-(3-aminopropyl)morpholine, and
 N,N-dimethyl-2-(2-aminoethoxy)ethanol.

46. The method of claim 43, wherein said nitrogen-containing carboxylic acid or imine is selected from the group consisting of:

- 10 iminodiacetic acid (IDA),
 glycine,
 nitrilotriacetic acid (NTA),
 hydroxyethyliminodiacetic acid,
 1,1,3,-tetramethylguanidine (TMG),
 15 ethylenediaminetetracetic acid (EDTA),
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,
 $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,
 $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$,

$\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$, and

$\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$.

47. The method of claim 43, wherein said metal chelating agent is selected from the group consisting of:

- 5 acetoacetamide;
- ammonium carbamate;
- ammonium pyrrolidinedithiocarbamate (APDC);
- dimethyl malonate;
- methyl acetoacetate;
- 10 N-methyl acetoacetamide;
- 2,4-pentanedione;
- 1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfac);
- 2,2,6,6-tetramethyl-3,5-heptanedione H(thd);
- tetramethylammonium thiobenzoate;
- 15 tetramethylammonium trifluoroacetate;
- tetramethylthiuram disulfide (TMTDS);
- lactic acid;
- ammonium lactate;
- malonic acid

formic acid,
acetic acid,
propionic acid,
gamma-butyrolactone,
5 methyl-diethanolammonium trifluoroacetate, and
trifluoroacetic acid.

48. The method of claim 43, wherein said fluoride source is selected from the group consisting
of: any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or
10 hydrofluoric acid,

ammonium fluoride,
ammonium bifluoride,
triethanolammonium fluoride (TEAF),
diglycolammonium fluoride (DGAF),
15 methyl-diethanolammonium fluoride (MDEAF),
tetramethylammonium fluoride (TMAF), and
triethylamine tris (hydrogen fluoride) (TREAT-HF).

49. The method of claim 43, wherein said organic amine is selected from the group consisting
20 of:

- diglycolamine (DGA),
methyldiethanolamine (MDEA),
pentamethyldiethylenetriamine (PMDETA),
triethanolamine (TEA),
5 triethylenediamine (TEDA),
hexamethylenetetramine,
3, 3-iminobis (N,N-dimethylpropylamine),
monoethanolamine.
2-(methylamino)ethanol,
10 4-(2-hydroxyethyl)morpholine
4-(3-aminopropyl)morpholine, and
N,N-dimethyl-2-(2-aminoethoxy)ethanol.

50. The method of claim 43, wherein said nitrogen-containing carboxyl acid or imine is selected
15 from the group consisting of:

iminodiacetic acid (IDA),
glycine,
nitrilotriacetic acid (NTA),
hydroxyethyliminodiacetic acid ,

1,1,3,3-tetramethylguanidine (TMG),

ethylenediaminetetracetic acid (EDTA),

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,

5 $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,

$(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$,

$\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$, and

$\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$.

10 51. The method of claim 43, wherein said fluoride source is selected from the group consisting of:

any combination of ammonia gas or ammonium hydroxide and hydrogen fluoride gas or hydrofluoric acid,

ammonium fluoride,

15 ammonium bifluoride,

triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),

methyldiethanolammonium fluoride (MDEAF),

tetramethylammonium fluoride (TMAF), and

20 triethylamine tris (hydrogen fluoride) (TREAT-HF);

said organic amine is chosen from the group consisting of:

- diglycolamine (DGA),
- methyldiethanolamine (MDEA),
- pentamethyldiethylenetriamine (PMDETA),
- 5 triethanolamine (TEA),
- triethylenediamine (TEDA),
- hexamethylenetetramine,
- 3, 3-iminobis (N,N-dimethylpropylamine),
- monoethanolamine.
- 10 2-(methylamino)ethanol,
- 4-(2-hydroxyethyl)morpholine
- 4-(3-aminopropyl)morpholine, and
- N,N-dimethyl-2-(2-aminoethoxy)ethanol;

said nitrogen-containing carboxylic acid or imine is chosen from the group consisting of:

- 15 iminodiacetic acid (IDA),
- glycine,
- nitrilotriacetic acid (NTA),
- hydroxyethyliminodiacetic acid,
- 1,1,3,-tetramethylguanidine (TMG),

ethylenediaminetetracetic acid (EDTA),

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$,

$\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$,

5 $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$,

$\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$, and

$\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$; and

said metal chelating agent is selected from the group consisting of:

acetoacetamide;

10 ammonium carbamate;

ammonium pyrrolidinedithiocarbamate (APDC);

dimethyl malonate;

methyl acetoacetate;

N-methyl acetoacetamide;

15 2,4-pentanedione;

1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(hfac);

2,2,6,6-tetramethyl-3,5-heptanedione H(thd);

tetramethylammonium thiobenzoate;

tetramethylammonium trifluoroacetate;

- tetramethylthiuram disulfide (TMTDS);
- lactic acid;
- ammonium lactate;
- malonic acid
- 5 formic acid,
- acetic acid,
- propionic acid,
- gamma-butyrolactone,
- methyldiethanolammonium trifluoroacetate, and
- 10 trifluoroacetic acid.

52. The method of claim 43, wherein said fluoride source comprises a compound having the formula $R_1R_2R_3R_4NF$ in which each of the R groups is hydrogen atoms or aliphatic, and wherein said metal chelating agent has the formula:

- 15 X-CHR-Y,

in which R is either hydrogen or an aliphatic group, and X and Y are functional groups containing multiply-bonded moieties having electron-withdrawing properties.

53. The method of claim 43, wherein said fluoride source comprises a compound having the
- 20 formula $R_1R_2R_3R_4NF$ in which each of the R groups is hydrogen or aliphatic, and wherein said

metal chelating agent has the formula, $R_1R_2R_3R_4N^+O_2CCF_3$ in which each of the R groups is hydrogen or aliphatic.

54. The method of claim 43, wherein said nitrogen-containing carboxylic acid has the formula:

5 $COOH-CH_2-NR^r$

Wherein each of r and r' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acid.

55. A method of removing residue from a wafer following a resist plasma ashing step on said
10 wafer, comprising contacting the wafer with a cleaning formulation, including (i) a fluoride source, (ii) at least one organic amine, (iii) a nitrogen-containing carboxylic acid or an imine, (iv) water, and optionally at least one metal chelating agent.

56. A wafer cleaning formulation, including (i) a fluoride source, (ii) at least one organic amine,
15 (iii) a nitrogen-containing carboxylic acid or an imine, (iv) water, and optionally at least one metal chelating agent.